

Pt, Au, Pd and Ru partitioning between mineral and silicate melts: The role of metal nanonuggets.

V. Malavergne¹ and², E. Charon², J. Jones³, A. Agranier⁴, A. Campbell⁵, ¹Université Paris Est-Marne La Vallée, Laboratoire des Géomatériaux et Environnement, Champs-sur-Marne, 77454 Cedex, France, ² Ecole Normale Supérieure de Paris, Laboratoire de Géologie, 24 rue Lhomond, 75005 Paris, France, ³ NASA Johnson Space Center, Houston, Texas 77058, USA, ⁴ IUEM, Université de Brest, France, ⁵Department of Geophysical Sciences, University of Chicago, 5734 S Ellis Av., Chicago, IL 60637.

Introduction The partition coefficients of Pt and other Pt Group Elements (PGE) between metal and silicate $D_{\text{Metal-Silicate}}$ and also between silicate minerals and silicate melts $D_{\text{Mineral-Silicate Melt}}$ are among the most challenging coefficients to obtain precisely. The PGE are highly siderophile elements (HSE) with $D_{\text{Metal-Silicate}} > 10^3$ (e.g., [1, 2]) due to the fact that their concentrations in silicates are very low (ppb to ppt range). Therefore, the analytical difficulty is increased by the possible presence of HSE-rich-nuggets in reduced silicate melts during experiments (e.g., [1, 2]). These tiny HSE nuggets complicate the interpretation of measured HSE concentrations. If the HSE micro-nuggets are just sample artifacts (e.g. [1, 2]), then their contributions should be removed before calculations of the final concentration. On the other hand, if they are produced during the quench [3], then they should be included in the analysis.

We still don't understand the mechanism of nugget formation well. Are they formed during the quench by precipitation from precursor species dissolved homogeneously in the melts, or are they precipitated in situ at high temperature due to oversaturation? As these elements are important tracers of early planetary processes such as core formation, it is important to take up this analytical and experimental challenge. In the case of the Earth for example, chondritic relative abundances of the HSE in some mantle xenoliths have led to the concept of the "late veneer" as a source of volatiles (such as water) and siderophiles (e.g., [1]) in the silicate Earth. Silicate crystal/liquid fractionation is responsible for most, if not all, the HSE variation in the martian meteorite suites (SNC) and Pt is the element least affected by these fractionations [4]. Therefore, in terms of reconstructing mantle HSE abundances for Mars, Pt becomes a very important player. In the present study, we have performed high temperature experiments under various redox conditions in order to determine the abundances of Pt, Au, Ru and Pd in minerals (olivine and diopside) and in silicate melts, but also to characterize the sizes, density and chemistry of HSE nuggets when present in the samples.

Experimental and analytical procedures. The starting materials used for the present work were terrestrial and martian basaltic glasses plus a mixture of (Au, Pt, Pd and Ru) metals. Experiments were performed using a vertical tube furnace which

allowed control of the $f\text{O}_2$ by gas mixing (CO/CO₂), and a rapid drop quench. A Pt-Rh thermocouple (Type B), calibrated against the melting point of gold, was used to monitor the temperature of the experiments. The oxygen fugacity of the samples was checked by using a remote zirconia oxygen cell. We performed experiments under air, pure CO₂, and near QFM. The samples were held in open crucibles fabricated from either diopside or San Carlos olivine monocrystals. The crucibles were suspended in the furnace with Pt wires. The samples were held at 1350°C for several days in order to reach equilibrium. Finally, the samples were drop-quenched into water.

Initial evaluation of experiments was performed using a JEOL JSM-5910LV Secondary Electron Microscope (SEM) and a Cameca SX-100 electron microprobe to determine the homogeneity of phases and to perform major/minor element analyses on crystals selected for Pt, Au, Ru and Pd analysis. Trace elements were determined using two different Thermo Finnigan Element HR-ICP-MS associated to a 193nm laser ablation inductively coupled plasma mass spectrometers (LA-ICP-MS). The LA-ICP-MS analyses were performed using techniques similar to those described by [5, 6]. With both instruments, measurements were calibrated using NIST 610 and 612 standards and 80 to 100 μm laser ablation diameters. Transmission Electron Microscopy (JEOL 2500SE) has been used to characterize some samples containing very small nuggets.

Results. In all samples, three main phases were characterized: the mineral of the crucible (olivine or diopside), the silicate glass and a two-phase metallic bead. The metallic matrix was Au-rich with few wt% of Pt and Pd, the second and minor metallic phase is a Pt-Ru alloy with traces of Au. These observations are in good agreement with the thermodynamic properties of Pt-Au-Pd-Ru (e.g. [7]). All experiments closely approached equilibrium, based on the fact that no compositional gradient was detected with the major elements, and also on $K_D(\text{Fe/Mg})$ and $K_D(\text{Ca/Mg})$ for olivine/liquid. The iron content of the glass decreased with the $f\text{O}_2$ of the experiment as expected. PGE nuggets have been observed in all our samples, even for the experiments with the most oxidized conditions (pure air). HSE nuggets were

characterized in the glass, on the boundary between the olivine or diopside, and also in the olivine or diopside, which was very surprising (Fig. 1). The size of these nuggets ranged from around 20 nm up to several μm . The chemical composition of the nuggets was not constant within a given sample. They were either made of Au-Pt alloys, pure Pt-Ru alloys, as well as pure Au and pure Pt. The nugget compositions were therefore not always linked to the composition of macroscopic two-phase metallic bead mentioned above.

Discussion. The presence of HSE micro-nuggets in both minerals (olivine or diopside, Fig. 1) and melts complicates the possible interpretation of their formation, but at the same time provides also new clues. First, their formations in our experiments were not obviously linked to a simple quench effect, as was the case in the very high temperature work of [3]. Indeed, if all the HSE nuggets observed in our samples were formed during quench, then they couldn't be in olivine or diopside grains since these minerals did not melt during the experiments. Secondly, quench nuggets would be spread homogeneously throughout the glass, but there are glass areas in all our experiments that were totally devoid of them (e.g. Fig. 1). Based on these results, we determined partition coefficients for Pt, Au, Pd and Ru between olivine and silicate melt and also between diopside and silicate melt at different fO_2 but only when HSE nuggets were absent from the ICPMS signals. Our results are in relatively good agreement with previous work (e.g. Fig. 2) for $D_{\text{olivine}-\text{Melt}}$ and confirm that these elements have generally a strong affinity for the silicate melt since $D_{\text{olivine}-\text{Melt}} < 1$ except for Au, which can approach 1. This work gave the first partition coefficients for $D_{\text{diopside}-\text{Melt}}$. But, clearly more data are needed to understand the behavior of these elements over a large range of fO_2 and temperatures. Regardless, we would not expect such a large variation in nugget composition if the nuggets formed during the quench. Further, we might even expect that the initial quench-nugget composition should approximate the compositions within our macroscopic metal bead (i.e., attempt to approach the composition of an equilibrium phase).

Finally, we have calculated that the contribution in the LA-ICP-MS time-resolved signal of the smallest Pt-rich-nugget (20 nm or so) could be less than 1% of the total measured material and may therefore not be easily recognized as peaks in the time-resolved spectra, underlining the importance of SEM (and TEM) characterization before LA-ICP-MS measurements for such samples.

References: [1] Fortenfant et al. (2006) Geochim.

Cosmochim. Acta 70, 742–756. [2] Erter et al, 2006 . 70 (2006) Geochim. Cosmochim. Acta 2591–2602 [3] Cottrell and Walker, 2006. Geochim. Cosmochim. Acta 70, 1565–1580 JH, Neal CR, Ely JC (2003) Chemical Geology, 196, 21-41. [4] Jones JH, Neal CR, Ely JC (2003) Chemical Geology, 196, 21-41. [5] Campbell A.J., Humayun M., Weisberg M.K. (2002) Geochim. Cosmochim. Acta, 66, 647-660. [6] Agranier and Lee (2007) Earth Planet. Sci. Lett. 257, 290-298. [7] Hultgren R., Desai P.T. Hawkins D.T., Gleiser M., Kelley K.K. (1973) American Society for Metals, Metal Park, Ohio.

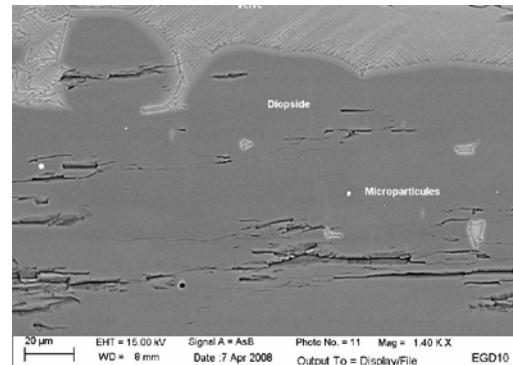


Fig. 1 : BSE image of a synthetic martian basalt heated at 1350°C during 4 days in diopside crucible. Pt-Ru-Nuggets are visible in diopside. The glass is the light gray phase at the top of the photo.

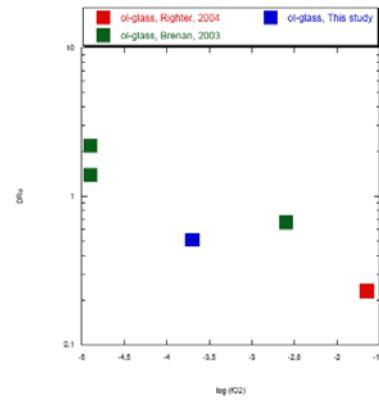


Fig. 2: The partition coefficients of Ru between olivine and melt from this study and previous works, are plotted vs fO_2 .